

SURPRISAL ANALYSIS OF ROTATIONAL–TRANSLATIONAL ENERGY TRANSFER: NON-LINEAR VERSUS LINEAR ROTORS *

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Surprisal versus energy gap analyses of state-to-state cross sections are presented for a number of linear rigid rotors excited by collisions with atoms: $\text{H}_2\text{--H}$, $\text{H}_2\text{--He}$, HCl--He , HCl--Ar , CO--He , CS--H_2 ($j=0$), OCS--H_2 ($j=0$), and $\text{HN}_2\text{--He}$. In all cases cross sections were obtained from accurate scattering calculations on realistic (theoretical) intermolecular potentials. All systems show the expected correlation between surprisal and reduced energy gap, i.e., the probability of rotational excitation decreases (relative to a statistical prior) with increasing inelasticity. However, different systems exhibit wide variability in the slope of the surprisal, and some show definite curvature. Also, all systems show more or less scatter in the surprisal plot, in some cases enough to indicate that the energy gap may not be the static dynamical constraint. Similar analyses are presented, for the first time, for some non-linear rotors excited by atoms: $\text{H}_2\text{CO--He}$ and $\text{H}_2\text{O--He}$. For these, the data show a great deal of scatter, indicating that the reduced energy gap is probably not the appropriate independent variable.

1. Introduction

Since its introduction into the field of molecular collision dynamics in the early 1970's information theory has found wide application. A good review of this work has been given recently by Levine [1]. A key feature of the information theoretic approach is its focus on the relationship of the actual (experimental or theoretical) rate constants or cross sections to reference or "prior expectation" values. This is expressed in terms of a surprisal, I , defined as

$$I = -\ln \sigma/\sigma^0, \quad (1)$$

where σ and σ^0 are the actual and prior cross sections, respectively. The surprisals, like the prior and actual cross sections, depend, in general, on the initial and final quantum states and the energy.

According to the orthodox interpretation, the prior cross sections are defined such that the probabilities of all energetically accessible final states are equal; this prior can be rationalized in terms of least bias, least information content, or maximum entropy. There have been some questions about the appropriateness of

this "statistical" prior. These are based on a well known problem in probability and statistics, which has been stated succinctly in a standard textbook as follows [2]: "The uniform model was used much more freely in the past than it is today, the simple results of an experiment being often quite uncritically treated as equally likely. The practice was justified by citing the principle of insufficient reason, which declared that cases were equally likely unless reasons to the contrary were known. Unfortunately, the results were often quite unrealistic since events might occur with quite different frequencies even though the model builder was unaware of the reasons for the difference." Such criticisms of information theory seem unwarranted since σ^0 is not intended as a model for the true cross sections, but rather as a reference point. By examining deviations from the prior (the surprisals) one hopes to find regularities which might indicate how the outcome is influenced by details of the actual dynamics. It therefore seems reasonable to adopt a prior which is not biased by any dynamic constraints, and the statistical prior will be used in the present work.

In the last decade much detailed data has been obtained about rotational–translational energy transfer in molecular collisions. This has come mainly from

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accurate theoretical calculations of state-to-state cross sections; for a recent review see, e.g., ref. [3]. A number of these results have been analyzed in terms of information theory. Most of the accurate theoretical cross sections to date have been obtained for the simplest case of a structureless atom colliding with a linear rigid rotor, and the surprisal analyses appear to have been confined entirely to this case. For a linear rotor colliding with an atom the surprisal depends on the initial and final quantum levels of the rotor, j and j' , respectively, and on the total (translational plus rotational) energy, E , and can be written as

$$I(j, j'|E) = -\ln w(j, j'|E), \quad (2)$$

where

$$w(j, j'|E) = (2j' + 1)^{-1} (E - E_j)^{1/2} (E - E_{j'})^{-1/2} \times a(j \rightarrow j'|E) \quad (3)$$

is symmetric in j and j' because of detailed balance. E_j is the rotational energy of the molecule in level j . It can be noted that exactly the same analysis applies to a symmetric or an asymmetric top rigid rotor colliding with an atom, except that the rotational energy levels then require quantum indices in addition to j ; however, these additional quantum numbers affect neither the rotational degeneracy nor the translational density of states.

It has often been argued [1] that a basic dynamical constraint in rotational-translation energy transfer is the energy gap, i.e., the amount of energy which must be converted from one degree of freedom to another. It is convenient to introduce the reduced energy gap,

$$\Delta f = (E_{j'} - E_j)/E, \quad (4)$$

since this is constrained by conservation of energy to vary between +1 and -1. [Because $w(j, j'|E)$ and hence $I(j, j'|E)$ are symmetric in j and j' , only $0 \leq |\Delta f| \leq 1$ need be considered.] Information theory then suggests that a plot of $I(j, j'|E)$ versus $|\Delta f|$ might show significant regularities. In the simplest case, such a surprisal plot would be linear, corresponding to an exponential decrease of the cross section with increasing energy gap. Such an "exponential gap law" for cross sections had been suggested previously by experimental measurements [4], and early information theoretic analyses seemed to indicate that it might have some generality.

Deviations of two kinds from a simple linear surprisal versus energy gap are possible. In the first, the reduced energy gap continues to be the appropriate independent variable insofar as it provides a smooth (single-valued) functional form for the surprisal, although the relationship need not be linear. Such deviations from linearity have already been noted for several systems [1]. In the second, use of the reduced energy gap as independent variable results in considerable scatter in the surprisal plot, i.e., different transitions with the same energy gap have differing surprisals. In his recent review, Levine states [1]: "At the moment additional examples are required to document this case".

Various dynamical effects can be considered which might lead to deviations from a linear surprisal versus energy gap plot. Dynamical constraints can be contemplated other than the ΔE constraint, for example, Δj constraints associated with conservation of angular momentum, a sort of "flywheel" effect. For a linear rotor, of course, ΔE and Δj are highly correlated. If the dynamics can be described by some combination of (or competition between) ΔE and Δj constraints, one predicts curvature in the surprisal versus energy gap plot, but relatively little scatter (i.e., the energy gap still serves as a good independent variable). For the more general case of an asymmetric top rotor, where ΔE and Δj are not well correlated, competition between ΔE and Δj constraints might lead to large scatter, as well as non-linearity, in a surprisal versus energy gap plot. Other dynamical effects which would cause scatter are known, in particular the "near homonuclear propensity" observed in some linear rotors. If the rotor has homonuclear symmetry, so that the angular dependence of the interaction potential is symmetric, only even Δj transitions are allowed. It has been well documented (see, e.g., Chapman and Green [5]) that even for some systems where the rotor does not have this symmetry, the interaction potential is *nearly* symmetric; and in such systems even Δj cross sections are much larger than odd Δj cross sections.

Surprisal analyses have been presented for translational-rotational energy transfer in a number of systems including (see ref. [1] for references to the original literature): H_2-H , H_2-He , H_2-Li^+ , $HD-He$, $CO-H$, CO_2-He , and N_2-Ar . The basic conclusions which were drawn from these studies can be summarized as follows: (1) the reduced energy gap appears to be the correct independent variable insofar as it leads to rela-

tively little scatter from a smooth functional dependence, and (2) while a linear functional form is adequate for some systems, others display varying amounts of curvature. There is some danger, however, in carrying these generalizations too far. First, the variety of systems considered to date is relatively limited; for example, none of the systems known to show "near homonuclear propensity" have been analyzed. Second, for many of the systems studied only a rather small number of state-to-state cross sections were available. Finally, scatter present in a surprisal plot tends to be masked due to the logarithmic relation between the surprisal and the cross section.

The purpose of the present study is to increase the data base for assessing surprisal analyses in two directions. First, for linear molecules, analyses are given for a number of systems not considered previously and also of more extensive results for some systems which were considered previously. Second, surprisal analyses are presented for the first time for some non-linear rigid rotors excited by collisions with atoms. The former are presented in section 2 and the latter in section 3. A summary of findings is in section 4.

2. Linear rotors

In this section surprisal analyses are presented for $\text{H}_2\text{-H}$, $\text{H}_2\text{-He}$, HCl-He , HCl-Ar , CO-He , CS-H_2 ($j=0$), OCS-H_2 ($j=0$), and $\text{N}_2\text{H}^+\text{-He}$. The notation H_2 ($j=0$) indicates that the hydrogen molecule was constrained to remain in its lowest, $j=0$ level, and hence it acts like a structureless, spherical atom. State-to-state cross sections for these systems have been obtained from extensive theoretical calculations. The intermolecular potentials were obtained in most cases from ab initio calculations, of varying levels of accuracy, and are believed to be quite realistic. Collision dynamics were treated within the accurate close coupling framework or, more often, within the coupled states approximation. For the latter cases, the approximate dynamics were tested by comparison with close coupling results at representative points and shown to be accurate to generally better than 20–30% for cross sections. All of the calculations used large, converged, rotational basis sets. Further details of the calculations for each system can be found in the original literature cited below.

Results for $\text{H}_2\text{-H}$ [6] at a total (translational plus rotational) energy of $10\,000\text{ cm}^{-1}$ are shown in fig. 1. Plotted here – and in all subsequent figures – is $w(j, j')$,

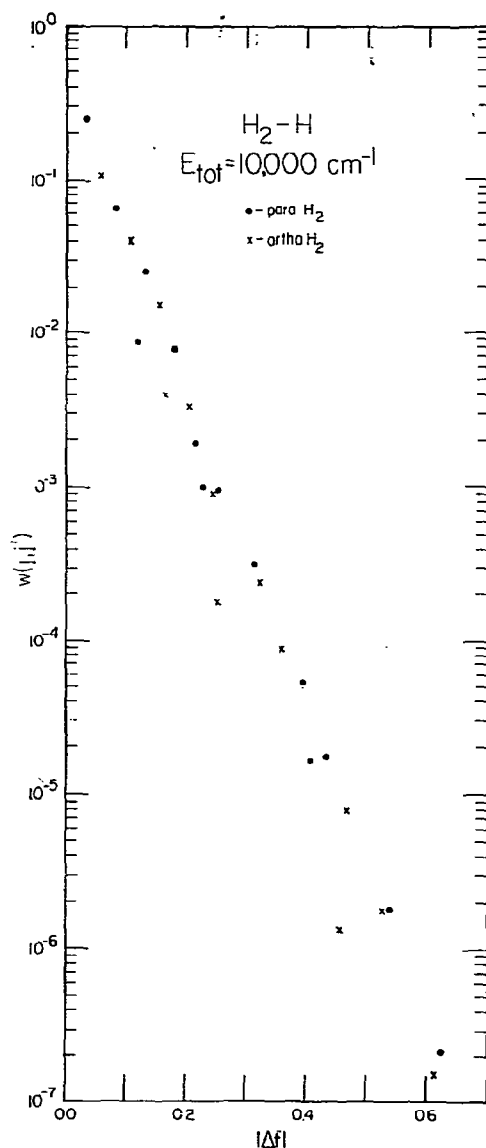


Fig. 1. Ratio of calculated to prior cross sections as a function of the reduced energy gap for H_2 excited by collisions with H atoms at a total energy of $10\,000\text{ cm}^{-1}$. Cross sections among the para- H_2 (even j) levels are indicated by dots, among the ortho- H_2 (odd j) levels by crosses.

eq. (3), versus the reduced energy gap $|\Delta f|$, eq. (4). The ordinate is a logarithmic scale, so that (cf. eq. (2)) the resulting plots are closely related to the standard surprisal plot; in particular, linearity and degree of scatter are identical in both methods of presentation. The present method of presentation has been chosen

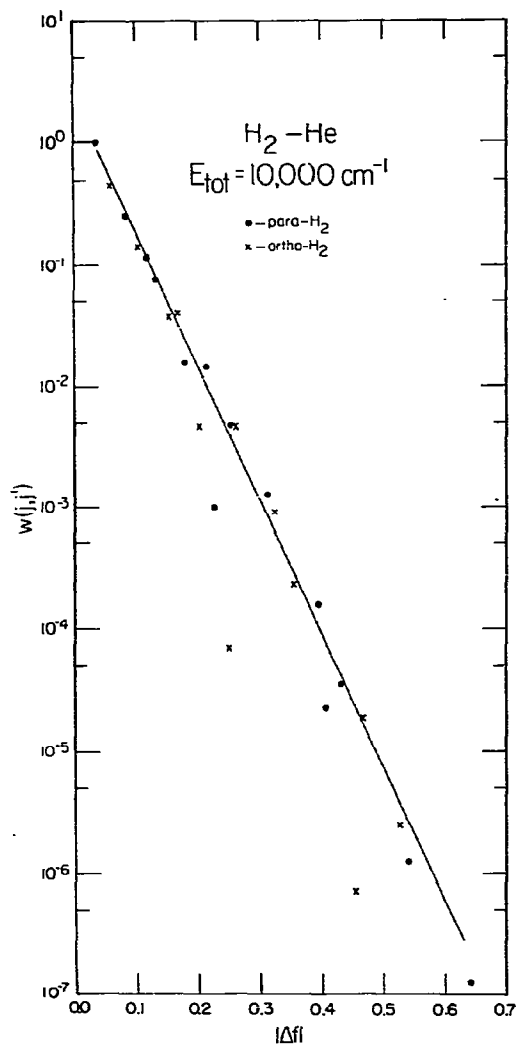


Fig. 2. Ratio of calculated to prior cross sections as a function of the reduced energy gap for H₂ excited by collisions with He atoms at a total energy of 10 000 cm⁻¹. Values for para-H₂ levels are indicated by dots, for ortho-H₂ levels by crosses. A straight line has been drawn for purposes of visualization only.

since $w(j, j')$ is more readily visualized in terms of a cross section, being just the cross section divided by the prior expectation. A fractional error in estimating $w(j, j')$, for example, due to deviations from a fit functional form, translates into the same fractional error in a cross section, $\sigma(j, j')$, predicted from this value. It can also be noted that $w = 1$ corresponds to the case where the total energy is divided "statistically" among translational and rotational energy in the final state; $w < 1$ implies less energy in rotation than this "prior expectation". The H₂-H data shown in fig. 1 include rotational levels to $j = 12$, i.e., all open levels. Transitions among para-H₂ (even) levels are indicated by dots, and among the ortho-H₂ levels by crosses. The most striking feature about fig. 1 is that the data are essentially linear with relatively little scatter, less than about a factor of five, despite the fact that the $w(j, j')$ vary by *seven orders of magnitude*. There is no apparent distinction between the para-H₂ and ortho-H₂ points. Fig. 2 presents data for H₂-He [7] at the same energy; these results are seen to be quite similar to those for H₂-H. The straight line in fig. 2 has been drawn as an aid to visualization only.

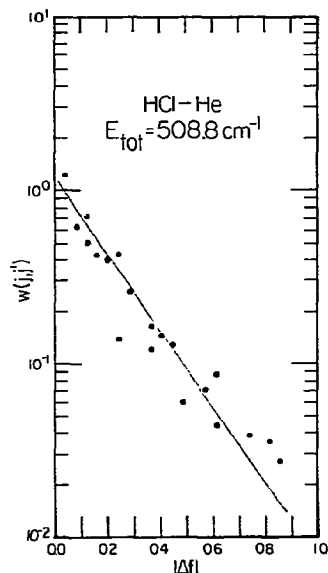


Fig. 3. Ratio of calculated to prior cross sections as a function of the reduced energy gap for HCl excited by collisions with He atoms at a total energy of 508.8 cm⁻¹. A straight line has been drawn for purposes of visualization only.

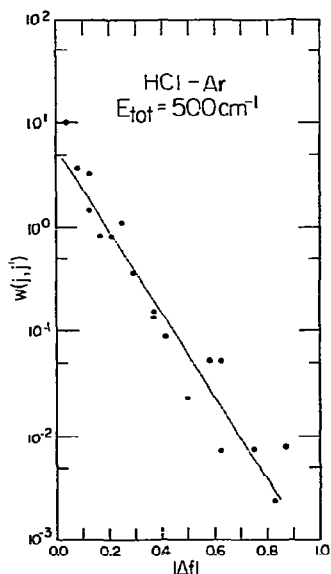


Fig. 4. Ratio of calculated to prior cross sections as a function of the reduced energy gap for HCl excited by collisions with Ar atoms at a total energy of 500 cm⁻¹. A straight line has been drawn for purposes of visualization only.

Fig. 3 presents data for HCl–He [8] at a total energy of about 500 cm⁻¹, and fig. 4 presents similar data for HCl–Ar [5]. In the former, cross sections among all open levels (though $j = 6$) are included; in the latter all cross sections with initial $j \leq 3$ are shown. For HCl–He, the range of $w(j, j')$ is only two orders of magnitude, in marked contrast to the H₂ systems. For HCl–Ar, $w(j, j')$ ranges over nearly four orders of magnitude, but this is still much less than in the H₂ systems. For both systems, the variation with $|\Delta f|$ is essentially linear, although the scatter is somewhat more pronounced here than for the H₂ systems. The straight lines in figs. 3 and 4 have been drawn as an aid to visualization only.

Figs. 5 and 6 show data for CO–He [9] at total energies of 120 cm⁻¹ and 400 cm⁻¹, respectively. Fig. 5 includes cross sections among all open levels (through $j = 7$); fig. 6 includes cross sections among levels through $j = 10$ although levels through $j = 13$ are open. This system has been discussed previously as an example of “near homonuclear propensity” so that the even Δj transitions (indicated in figs. 5 and 6

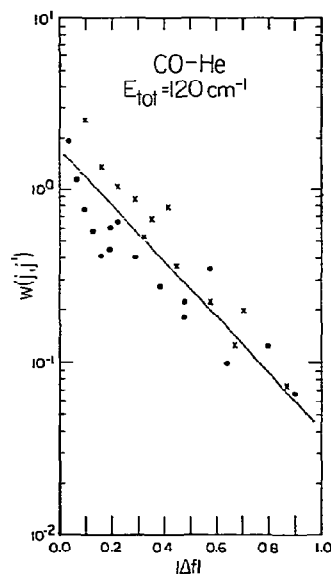


Fig. 5. Ratio of calculated to prior cross sections as a function of the reduced energy gap for CO excited by collisions with He atoms at a total energy of 120 cm⁻¹. Odd Δj transitions are indicated by dots, even Δj transitions by crosses. The straight line has been drawn for purposes of visualization only.

by crosses) are generally larger than adjacent odd Δj transitions (indicated by dots). This trend is clearly evident in figs. 5 and 6 for small $|\Delta f|$. However, it is known that this “homonuclear propensity” reverses for larger Δj transitions [10] (induced by higher order interactions of the potential), and this is also apparent in the data shown here at larger $|\Delta f|$. At the lower energy (fig. 5) a linear dependence on $|\Delta f|$ seems reasonable; at the higher energy (fig. 6), however, a definite curvature, especially at smaller $|\Delta f|$, is apparent. The results for CO differ from the H₂ systems discussed above insofar as the total range of $w(j, j')$ values is much more limited, only about two orders of magnitude. Therefore the scatter in the data – about a factor of three – appears relatively more important.

Fig. 7 presents results for CS–H₂ ($j = 0$) [9] at a total energy of 105 cm⁻¹. Cross sections among all open levels (through $j = 10$) are included. As with the previous systems, $w(j, j')$ is seen to decrease, covering a range of nearly three orders of magnitude, with in-

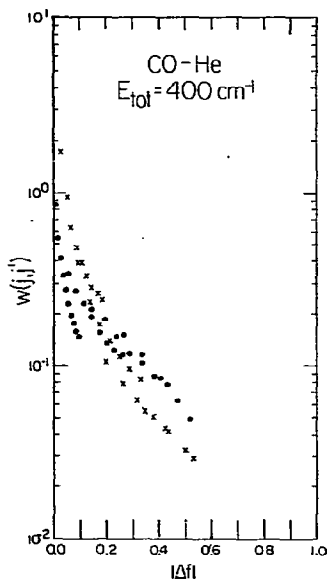


Fig. 6. Ratio of calculated to prior cross sections as a function of the reduced energy gap for CO excited by collisions with He atoms at a total energy of 400 cm^{-1} . Odd Δj transitions are indicated by dots, even Δj transitions by crosses.

creasing $|\Delta f|$. The straight line in fig. 6 has been drawn only as an aid to visualization; the data would probably be better described by a curve, as the slope seems larger at small $|\Delta f|$ than at larger $|\Delta f|$. However, the scatter in these data is large enough — about a factor of five — to preclude an unambiguous choice of functional form.

Results for OCS- H_2 ($j=0$) [9] are presented in fig. 8. Cross sections among levels through $j=12$ are included, although levels through $j=22$ are open at the total energy of 100 cm^{-1} shown. This system shows a strong “near homonuclear propensity” which can be seen in fig. 8 by comparing the odd Δj transitions (dots) with the even Δj transitions (crosses). As for CO-He, the relative size of even and odd cross sections reverses for large Δj (large $|\Delta f|$). The $w(j, j')$ are seen to decrease strongly with $|\Delta f|$, showing some curvature. However, there is quite a bit of scatter — nearly an order of magnitude. Much of the scatter persists, especially at intermediate $|\Delta f|$, even if even and odd Δj transitions are considered separately. It should be noted that the dynamical calcula-

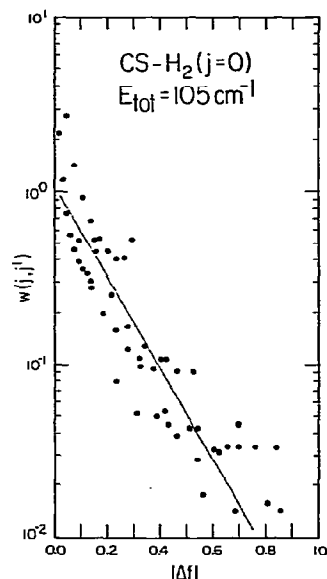


Fig. 7. Ratio of calculated to prior cross sections as a function of the reduced energy gap for CS excited by collisions with H_2 at a total energy of 105 cm^{-1} . The H_2 molecules have been constrained to their lowest, $j=0$ level and so act as spherical particles. The straight line has been drawn for purposes of visualization only.

tions here included rotational levels through $j=26$ which is thought to be adequate to converge all cross sections shown; hence the scatter cannot be attributed to erroneous dynamics.

Results for the final linear system considered here, $\text{N}_2\text{H}^+-\text{He}$ [11], are shown in fig. 9. The total energy is 80 cm^{-1} , and cross sections among all open levels (through $j=6$) are included. This system appears somewhat different from those considered above. After an initial drop in $w(j, j')$ for $|\Delta f| \leq 0.2$, the values remain relatively constant at $w(j, j') \approx 2$. It is interesting that such behavior for this system might have been inferred from earlier observations of the cross sections [11]: “the essentially statistical probability of different quantum transitions in N_2H^+ is attributed to the formation of relatively long-lived collision complex for the ionic ... system.” This, in turn, is due to a much deeper potential well, some 400 cm^{-1} which can be compared with the collision energy of 80 cm^{-1} .

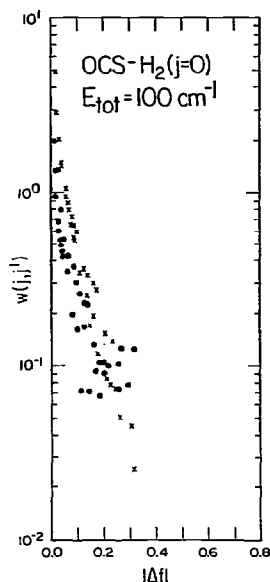


Fig. 8. Ratio of calculated to prior cross sections as a function of the reduced energy gap for OCS excited by collisions with H_2 at a total energy of 100 cm^{-1} . The H_2 molecules have been constrained to their lowest, $j = 0$ level and so act as spherical particles.

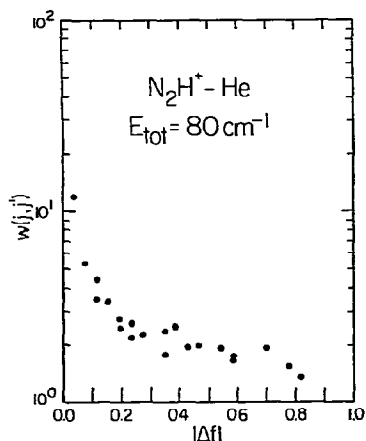


Fig. 9. Ratio of calculated to prior cross sections as a function of the reduced energy gap for the molecular ion N_2H^+ excited by collisions with He atoms at a total energy of 80 cm^{-1} .

3. Non-linear rotors

In this section surprisal analyses are presented for $\text{H}_2\text{CO}-\text{He}$ and $\text{H}_2\text{O}-\text{He}$. For both of these systems theoretical intermolecular potentials have been computed, and state-to-state cross sections have been obtained from extensive coupled states calculations (this dynamical approximation was shown to be accurate to generally 10–20% for cross sections by comparisons with limited close coupling calculations for both systems). Details of these calculations can be found in ref. [12] for $\text{H}_2\text{CO}-\text{He}$ and in ref. [13] for $\text{H}_2\text{O}-\text{He}$.

Formaldehyde is a near symmetric top. Rotational levels are described by quantum numbers j , which corresponds approximately to rotational motion of the C–O axis, and k , which corresponds approximately to spinning of the hydrogens about the C–O axis. Due to the small moment of inertia of the hydrogens, changes in k require significantly more energy than changes in j . Due to symmetry the levels separate into para- H_2CO (even k) and ortho- H_2CO (odd k). Results for ortho- $\text{H}_2\text{CO}-\text{He}$ at a total energy of 66.14 cm^{-1} are shown in fig. 10. At this energy only levels with

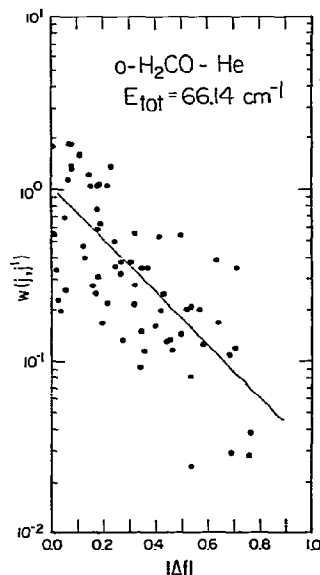


Fig. 10. Ratio of calculated to prior cross sections as a function of the reduced energy gap for ortho- H_2CO excited by collisions with He at a total energy of 66.14 cm^{-1} . A straight line has been drawn for purposes of visualization only.

$k=1$ and $j=1, 6$ are energetically accessible; each j, k level is split by the small asymmetry into closely spaced doublets. Fig. 10 includes cross sections among all open levels. As for the linear rotors, $w(j, j')$ (cf. eqs. (2) and (3)) is plotted here on a logarithmic scale versus the reduced energy gap, $|\Delta f|$ (cf. eq. (4)). There appears to be a general decrease in $w(j, j')$ with increasing $|\Delta f|$; a straight line has been drawn in fig. 10 for purposes of visualization only. However, there is a great deal of scatter in this plot; for a given value of $|\Delta f|$, $w(j, j')$ values vary by typically an order of magnitude. Since the entire range of $w(j, j')$ values is only two orders of magnitude, it is not clear that this data indicates significant correlation between $w(j, j')$ and $|\Delta f|$.

Results for $\text{H}_2\text{O}-\text{He}$ are shown in figs. 11 and 12 for total energies of 300 cm^{-1} and 600 cm^{-1} , respectively. As for formaldehyde, the rotational levels of water separate into para- H_2O and ortho- H_2O which are not connected by collisions. Cross sections among all open ortho- H_2O levels are shown in figs. 11 and 12 (nine levels at the lower energy and 19 levels at the higher energy). Again, there is a general trend of de-

creasing $w(j, j')$ with increasing $|\Delta f|$. However, the scatter in the data points for this system is even greater than for $\text{H}_2\text{CO}-\text{He}$, and it is not entirely clear that $|\Delta f|$ is an appropriate independent variable here.

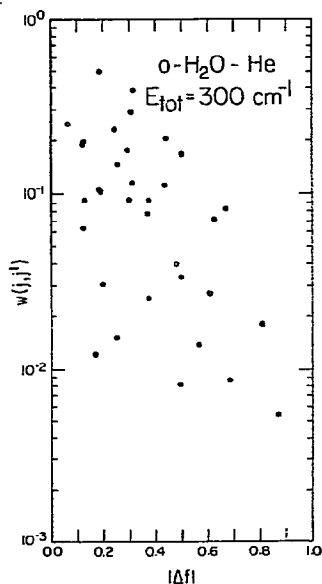


Fig. 11. Ratio of calculated to prior cross sections as a function of the reduced energy gap for ortho- H_2O excited by collisions with He atoms at a total energy of 300 cm^{-1} .

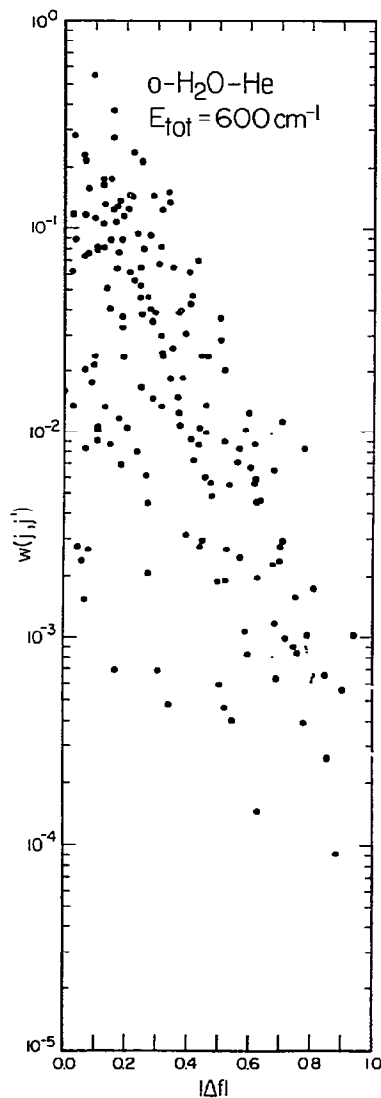


Fig. 12. Ratio of calculated to prior cross sections as a function of the reduced energy gap for ortho- H_2O excited by collisions with He atoms at a total energy of 600 cm^{-1} .

4. Discussion

The surprisal analyses for linear molecules presented in section 2, along with analyses for other systems published elsewhere, cover a wide enough range of collision parameters that one can begin to discuss general trends. Perhaps the most interesting question to consider, since it has formed the basis of much previous discussion, is whether the reduced energy gap, $|\Delta f|$, provides an appropriate independent variable. The evidence does, in fact, seem to imply that the variation in surprisal correlates relatively well with $|\Delta f|$, although perhaps not so well as had been inferred from some of the earlier studies. In all cases the observed trend follows the conventional expectation that the probability of rotational excitation decreases with increasing fraction of energy which must be converted from one degree of freedom to another (compared with a “statistical” redistribution of energy). Whether this correlation implies that the reduced energy gap is the fundamental dynamical constraint, as has often been suggested in information theoretic analyses, however, is not so apparent. For example, as discussed in the introduction, for a linear rotor the energy gap is correlated with Δj ; thus one might expect similar surprisal versus energy gap plots if the latter, rather than the former, provided the basic dynamical constraint. As also noted in the introduction, the curvature in these plots which is seen for several of the systems studied is consistent with combined ΔE and Δj dynamical constraints.

That the energy gap cannot be the entire story is indicated by the scatter which is present to a greater or lesser degree in all surprisal versus energy gap plots. One might hope to find trends in the rather extensive set of data presented here that would give clues about the dynamical constraints which do underlie the observed variation in surprisals. Although an exhaustive attempt to do this has not been made in the present study, several plausible correlations have been explored. Unfortunately, no regularities of general validity have been found. As discussed above, a number of linear molecule – atom collision systems are known to show a “near homonuclear propensity”, which introduces a certain amount of scatter into a surprisal versus energy gap plot since transitions with even Δj are more likely than those with odd Δj . One might hope that much of this scatter could be eliminated by

using separate plots for the even and odd transitions. For CO–He (figs. 5 and 6) and OCS–H₂ (fig. 8), both of which are known to show a strong “near homonuclear propensity”, this has been done, with the conclusion that it gives only a small reduction in the scatter.

A next obvious step would be to consider each Δj separately. For a linear molecule, within each Δj set $|\Delta f|$ increases regularly with increasing j , so that such a subset of the surprisal points defines, of necessity, a single-valued function, and the question then becomes whether this is a smooth function and whether there is a relationship connecting different Δj sets. Such an analysis does seem potentially useful, at least for some of the systems considered here. Perhaps one of the most striking examples of this is the CO–He data shown in fig. 6. Although it is not specifically indicated in the figure, an examination readily reveals smooth sets of points which correspond to $\Delta j = 1, 2, 3$, etc. Each Δj set shows a different slope and curvature, and regularities among these are not readily apparent. Also, since these calculations did not include all open rotational levels, it is not clear whether this regularity persists throughout the range of j values. The H₂ systems also seem to show greater regularity when different Δj sets are considered separately, although at higher j values in some sets the behavior is less regular. The data for the HCl systems, CS–H₂, and N₂H⁺–He, on the other hand, do not seem to lend themselves as well to an analysis based on Δj .

It is worthwhile to consider the degree to which a surprisal versus energy gap analysis might be useful in predicting state-to-state cross sections from a limited amount of information, for example, from cross sections out of one or a few initial levels or from the moments of the energy transfer. The first problem which must be faced in any such procedure is the variability among molecular systems in the slope of $w(j, j')$ as a function of $|\Delta f|$. For N₂H⁺–He, $w(j, j')$ drops by less than an order of magnitude, and, over most of the range of $|\Delta f|$, by only a factor of two; for H₂–He, on the other hand, it varies by seven orders of magnitude. Therefore, any successful procedure requires sufficient information for a given system to predict the range of $w(j, j')$. The second problem which must be faced is the scatter which appears to be inherent in a surprisal versus energy gap plot. Unless some more sophisticated procedure is used, for example,

one which considers variation among different Δj transitions, predictions of cross sections to better than about a factor of two cannot, in general, be expected, and this assumes the most favorable case, i.e., that the best fit line (or curve) to the entire cross section matrix has been obtained based on the limited input information. Inspection of figs. 1–9 suggests a further difficulty. Due to the scatter in the plots, it seems likely that a line (or curve) fit to some (small) subset of the points may not be representative of the entire set of points, and, in fact, could be quite different from the best fit to the whole set. It would therefore seem that state-to-state cross sections predicted from this kind of analysis cannot, at the present level of understanding, be expected to be accurate to better than an order of magnitude, except, perhaps, for a system where a fair amount of detailed information is already available.

The discussion above is based only on analyses of linear rotors; non-linear rotors, which have been examined for the first time in the present work, present a different story. Although the data for H_2CO and H_2O presented in figs. 10–12 show some indication that $w(j, j')$ decreases – at least on the average – with increasing $|\Delta f|$, the scatter in these plots suggests that the energy gap is not the dominant dynamical constraint in these systems. No attempt has been made here, however, to find a better independent variable for these systems. In view of the rather limited success discussed above in systematizing the scatter in the linear rotor data, it is not clear that such attempts would be profitable for the much more complicated non-linear systems.

It would appear, in conclusion, that quantitative details of state-to-state cross sections are the result of a complicated competition among different dynamical effects including the energy gap, the change in angular momentum, and the shape of the interaction. A surprisal analysis is undoubtedly useful in elucidating the effect on cross sections of these different dynamical constraints by removing purely statistical factors,

such as the rotational degeneracy and the translational density of states. At the current time, however, it appears naive to suggest that the variety of behavior possible for the whole range of collision systems can be *quantitatively* described in terms of a simple dependence on one or even a few of the dynamical parameters. On the other hand, it is encouraging that such analyses are able, at least for some systems, to properly account for the underlying qualitative trends.

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References

- [1] R.D. Levine, *Ann. Rev. Phys. Chem.* 29 (1978) 59.
- [2] J.L. Hodges and E.L. Lehmann, *Basic concepts of probability and statistics* (Holden-Day, San Francisco, 1964) p. 22.
- [3] J.P. Toennies, *Ann. Rev. Phys. Chem.* 27 (1976) 225.
- [4] J.C. Polanyi and K.B. Woodall, *J. Chem. Phys.* 56 (1972) 1563.
- [5] S. Chapman and S. Green, *J. Chem. Phys.* 67 (1977) 2317.
- [6] S. Green and D.G. Truhlar, *Astrophys. J.*, to be published.
- [7] S. Green, R. Ramaswamy and H. Rabitz, *Astrophys. J. (Suppl.)* 36 (1978) 319.
- [8] S. Green and L. Monchick, *J. Chem. Phys.* 63 (1975) 4198.
- [9] S. Green and S. Chapman, *Astrophys. J. (Suppl.)* 37 (1978) 169.
- [10] C.W. McCurdy and W.H. Miller, *J. Chem. Phys.* 67 (1977) 463.
- [11] S. Green, *Astrophys. J.* 201 (1977) 366.
- [12] S. Green, B.J. Garrison, W.A. Lester and W.H. Miller, *Astrophys. J. (Suppl.)* 37 (1978) 321.
- [13] S. Green, *Astrophys. J. (Suppl.)*, to be published.